



---

# Basic Ceramic Considerations for Lost Wax Processing of High Melting Alloys

*By H. Frye, Techform, M. Yasrebi & D.H. Sturgis,  
PCC Structural, Inc.*

©2011 The Bell Group, Inc. All rights reserved.

---

800.545.6566

riogrande.com



THE **studio**  
Rio's blog



# Basic Ceramic Considerations for Lost Wax Processing of High Melting Alloys

H. Frye\*, M. Yasrebi<sup>+</sup> and D. H. Sturgis<sup>+</sup>  
\*Techform, Milwaukie, OR;  
<sup>+</sup>PCC Structural, Inc., Portland, OR, USA

## Abstract

The growing demand for high melting alloys has led to the need for increasingly more refractory mold materials for the lost wax process. These materials must sustain their chemical, as well as mechanical, stability in order to produce high-quality castings. This paper initially outlines the mold requirements for a number of high temperature alloys. Ceramic-liquid metal interactions, oxygen affinity, as well as aqueous solution chemistry for multi-component refractory systems will be discussed. Next, guiding principles in practical mold design for the above alloys will be outlined.

## Introduction

The demand for casting high melting alloys has grown in recent decades due to attractive thermal, mechanical and chemical properties of such alloys. Since its initial development in the late 1940s/early 1950s, the lost wax process has enjoyed a healthy growth in the casting of high melting alloys in many markets, including aerospace, prosthetic, jewelry, automobile parts, hand tools and leisure equipment.

The casting of high melting alloys presents a special problem due to the high reactivity of these materials in the molten state. This reactivity requires special shell-making practices to reduce the introduction of casting defects. Specifically, shell materials need to be of sufficiently high refractoriness. As a general practice, a high refractory facecoat slurry is normally applied to the wax pattern to improve refractoriness. Shells need to have sufficient high-temperature mechanical stability to ensure dimensional accuracy of cast parts as well. Therefore, shells should neither densify nor creep throughout the process.

The need for use of high refractory shell molds imposes additional challenges to high melting alloy casting. Slurries made of high refractory flours may have a very short lifetime. Lack of sufficient slurry life can make the shell-making process more costly. Moreover, the quality of shells may become unsatisfactory even in batch processes.

The purpose of this paper is to outline a methodology for the design of ceramic shell mold systems suitable for casting high melting alloys.

## Thermodynamic Considerations

The general chemical reactions that lead to metal-mold reaction can be classified as being of the following types:



where  $M_xO_y$  denotes an oxide,  $\underline{M}$  and  $\underline{O}$  dissolved metal and oxygen in the alloy respectively,  $MA$  an element in the alloy, and  $(g)$  a gaseous species. The discussion that follows may also be extended to include carbides, nitrides, sulfides and borides as well.

Most high-temperature molten alloys dissolve molds to some extent. Reaction (1) describes dissolution of shell material into the liquid metal. The change in free energy for reaction (1) is equal to:

$$\Delta G = \Delta G_f^\circ, M_xO_y + RT \ln (a_{\underline{M}})^x (a_{\underline{O}})^y \quad (7)$$

where  $a_{\underline{M}}$  and  $a_{\underline{O}}$  are the activity coefficients of  $M$  and  $O$  in liquid metal respectively. Calculating the precise value of  $\Delta G$  in equation (7) is difficult. The activity coefficients are unknown, the conditions are non-standard, and the shell material is normally inhomogeneous. However, as a first order approximation, the solubility of various oxides in molten alloy decreases as  $\Delta G_f^\circ, M_xO_y$  becomes increasingly negative <sup>(1)</sup>.  $\Delta G_f^\circ$  for some commonly used refractory materials, as well as oxides of some high temperature metals are given in Figure 1. Data in Figure 1 suggests that it is unlikely that high refractory oxides dissolve into molten Pd or Pt metals according to equation 1. However, casting of Ti in oxide shell molds such as  $Al_2O_3$  or  $ZrO_2$  will result in substantial dissolution of oxygen and metal into molten Titanium. According to Figure 1,  $\Delta G_f^\circ$  of both  $Al_2O_3$  or  $ZrO_2$  are more negative than  $TiO_2$ . However,  $\Delta G_f^\circ$  of sub-oxides of Ti (*i.e.*,  $TiO$ ) are more negative than the above oxides. Therefore, one can predict that molten Ti is apt to react with mold materials. There are a few known refractory oxides for which the  $\Delta G_f^\circ$  is more negative than  $TiO$  <sup>(2-4)</sup>. Among these refractories,  $Y_2O_3$  has received particular attention as a serious candidate for Ti casting <sup>(5-6)</sup>. Figure 2 compares the level of surface oxygen ( $\alpha$  case) on cast titanium versus the type of oxide used as facecoat

material. Experimental details are given elsewhere <sup>(7)</sup>. The above data clearly shows the usefulness of  $\Delta G_f^\circ$  argument in evaluating the solubility of shell materials. Similar arguments have been used to show the solubility of oxides in superalloys as well <sup>(8-9)</sup>.

Reactions 2, 3 and 4 characterize the reaction of the molten metal with the mold. Reaction 2 becomes especially important when the gaseous reaction products have an appreciable equilibrium vapor pressure. Some of the most stable vapor oxide species commonly encountered in high melting alloys are listed in Figure 1. An example of reaction 2 is rapid decarborization of NiTaC alloy based on the following reaction:



Reaction 3 involves reduction of the mold by the metal to form another metal oxide. This type of reaction can also be predicted by comparing the  $\Delta G_f^\circ$  of mold material and oxide of molten metal. Thus, ignoring the contribution of activity coefficients, reaction 3 can be prevented/promoted by using mold materials having a  $\Delta G_f^\circ$  substantially more/less negative than oxide of molten metal respectively. A good example of reaction 3 is the reaction among Ti, Al or Hf in superalloys with the mold oxides <sup>(5)</sup>. The above reactions normally produce thin layers of molten metal oxide at the metal-mold interface. Such interfacial reactions are commonly stable and may be beneficial for the cast part by hindering further reactions between mold and the molten metal. Another example of reaction 3 is the reaction between Ti and the mold oxides in molten Ti alloys to form TiO or TiO<sub>2</sub>. The above oxides are frequently not seen because these oxides dissolve rapidly in metal.

Molten metal may form double oxides with the mold material (reaction 4). An example is the reaction between Al and rare earth oxides.  $\Delta G_f^\circ$  of rare earth oxides is normally more negative than  $\Delta G_f^\circ$  of alumina. Thus,  $\Delta G_f^\circ$  of double oxides comprised of Al<sub>2</sub>O<sub>3</sub> and a rare earth oxide are more negative than pure Al<sub>2</sub>O<sub>3</sub> <sup>(10)</sup>. For example, as shown in Figure 1,  $\Delta G_f^\circ$  of double oxides Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, YAlO<sub>3</sub> and YAl<sub>12</sub>O<sub>9</sub> are more negative than  $\Delta G_f^\circ$  of Al<sub>2</sub>O<sub>3</sub>. Consequently, molten Al is more reactive with rare earth shell molds than it appears to be on the basis of single oxide  $\Delta G_f^\circ$  data.

Reaction 5 characterizes a gaseous reaction product in a cast part. An example of such reaction is shown by Ingo and co-workers <sup>(11)</sup>. The authors show that CaSO<sub>4</sub>-SiO<sub>2</sub> mold materials used for casting alloys of Au or Pd decompose according to the following reactions:



The produced oxygen dissolves into the alloy and forms oxides with the minor alloying elements such as Cu, Ag and Zn. The above reaction is then further catalyzed by the presence of SiO<sub>2</sub> and the formed oxides in the melt. The result is the formation of a heavy concentration of SO<sub>2</sub> gas in the cast.

Reaction 6 represents solid to liquid transformation of ceramic components in the shell mold. Formation of liquid phase is detrimental to a cast part in a number of ways. Solid to liquid transformation does not contribute to a substantial change in the  $\Delta G_f^\circ$  of oxides <sup>(12)</sup>. However, formation of liquid phase increases the oxide mobility. Consequently, the kinetics of reactions increases. Formation of liquid phase lowers the mechanical stability of the shell mold as well. Surface erosion, part deformation and metal penetration into the mold can be among the many negative consequences of liquid formation. Table 1 compares the melting temperature of commonly used refractory oxides with some high temperature metals. As a general rule, shell material should be chosen such that its melting temperature is considerably above the melting temperature of the metal. Ceramic shell molds are multi-component systems. Consequently, the onset of liquid phase formation generally is lower than the melting temperature of individual pure oxides. For example, addition of Y<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub> reduces the onset of liquid phase formation from 1720°C to 1660°C. Addition of Al<sub>2</sub>O<sub>3</sub> to the above mixture will further reduce the liquidus temperature to 1370°C. The effect of fluxing agents needs to be considered as well. For example, conventional colloidal silica used in the lost wax process may contain more than 0.6 weight % of Na<sub>2</sub>O <sup>(13)</sup>. The added Na<sub>2</sub>O reduces the melting temperature of SiO<sub>2</sub> from 1720°C to as low as 837°C.

## Mold Surface Penetration

Beside cast defects caused by chemical reactions between the mold and the molten metal, physical interaction between mold and molten metal can also cause cast defects. Positive rough surface defects may be produced when molten metal penetrates into a mold porosity. The interaction between shell pores and molten metal can be approximated by: <sup>(14)</sup>

$$P = -2\gamma_{lv}\cos \theta/r \quad (10)$$

where P is the pressure necessary to force molten metal into a pore of radius r.  $\gamma_{lv}$  is the surface tension of the molten metal, and  $\theta$  is the contact angle between the molten metal and the shell.

Contact angles <90° indicate capillary attraction. Molten metal wets the mold and penetrates into the pore without an applied pressure. Contact angles >90° indicate non-wetting condition, and applied pressure P is necessary to force the molten metal into the pore. Contact angle  $\theta$  is related to surface and

interfacial energies according to Young's equation <sup>(14)</sup>:

$$\cos\theta = \gamma_{sv} - \gamma_{sl} / \gamma_{lv} \quad (11)$$

where  $\gamma_{sv}$  is the surface tension of refractory and  $\gamma_{sl}$  is the interfacial tension between the refractory and the molten metal. In order to promote metal penetration,  $\gamma_{sv}$  should be maximized and both  $\gamma_{sl}$  and  $\gamma_{lv}$  should be minimized. Interfacial tension,  $\gamma_{sl}$ , is perhaps the most influential factor in the value of contact angle between molten metal and the mold.  $\gamma_{sl}$  normally becomes lower upon the occurrence of an interfacial chemical reaction. Therefore, high-temperature reactive metal alloys such as Ti are more prone to cause metal penetration compared to less reactive metals such as Pt. Li <sup>(15)</sup> has also shown that surface tension of an oxide is directly related to its  $\Delta G_f^\circ$ . The above author shows that contact angle between molten Co, Fe or Ni and a mold changes from about 85° to nearly 135°, as the refractory changes from Cr<sub>2</sub>O<sub>3</sub> to an oxide with a more negative  $\Delta G_f^\circ$ , such as CaO.

Note that in equation 10,  $r$  is in the denominator. Therefore, the larger the radius, the smaller the pressure that is required to force the metal into the pore. Porosity in a lost wax shell mold is normally very fine. Therefore, in most situations, mechanical penetration of metal into the mold does not happen. However, under some conditions metal penetration becomes possible. Occurrence of chemical reaction between metal and mold normally reduces the contact angle below 90° and metal penetration becomes favorable. Moreover, formation of either liquid phase or occurrence of microcracks on the surface of the shell mold drastically increases the effective radius of porosity. Casting method can also have a major effect in promoting metal penetration. In static casting,  $P$  is primarily due to metallostatic head of the metal in the mold. However, metal pressure substantially increases in centrifugal casting and frequently causes metal finning in microcracked molds.

## Shell-Making Considerations

Proper selection of shell mold material is vital to the successful production of high-quality cast parts. However, it should be noted that the actual reaction of molten metal with the mold material is much rarer than supposed. Many of the observed defects in a cast part are actually a result of faulty shell mold production. In the following, some of the fundamentals of shell-making will be considered.

The lost wax shell-making process for high temperature alloys can be summarized in the following generalized steps.

- (A) Multi-component slurries are prepared. These slurries are composed of a refractory system and a binder system. The binder system includes at least one condensable inorganic binder.
- (B) Facecoat layer(s) are constructed through dip coating and stuccoing of an organic based pattern.
- (C) Shell mold is constructed either by applying multiple dip coatings, or by gelling a solid body of slurry around the facecoat layers.

If the slurry is an aqueous based slurry, the binder system generally includes a nano-meter-size colloidal silica binder. If the slurry is a non-aqueous-based slurry, the binder system is generally a silicon alkoxide. In either case, condensation of binders causes permanent siloxane bond formation upon shell drying <sup>(16)</sup>.

### ***a. Aging of slurries***

Because of the very nature of the shell-making process, slurries go through aging. As slurries age, they lose their useful properties, and either become useless, or jeopardize the quality of lost wax shell molds.

There are at least two reasons why lost wax slurries age <sup>(7)</sup>. First, different components in a slurry may interact with each other, and cause aging over time. For example, it has been shown that in aqueous slurries, the soluble species originating from each component of a slurry may specifically adsorb on the surface of other components <sup>(17-18)</sup>. Surface adsorption may modify surface properties and cause aging over time. The degree of interaction among different components of a slurry differs from one slurry to another. For example, as shown in Figure 3, aqueous MgO slurry with colloidal silica binder at pH 10.5 ages very rapidly and gels in less than an hour. Y<sub>2</sub>O<sub>3</sub> slurry under similar conditions gels in a few hours. On the other hand, Al<sub>2</sub>O<sub>3</sub> slurry under identical conditions remains stable for many months. Details of experimental procedures are given elsewhere <sup>(7, 17)</sup>. The above aging mechanism is shown to be the dissolution of polyvalent cationic ions from oxide flours, and then preferential adsorption of these ions on the surface of negatively charged colloidal silica particles <sup>(7, 17)</sup>.

The above diversely different aging behaviors among slurries can be predicted from a prior knowledge of the speciation diagram for each flour in an aqueous environment. Figure 4 compares the dissolution of yttria, magnesia and alumina. For simplicity, only the most dissolving ion specie from each flour is compared. At pH 10.5, dissolution of alumina is about five orders of magnitude lower than that of yttria. Consequently, stable alumina slurries can be made at pH 10.5. On the other hand, magnesia dissolves over three orders of magnitude higher than yttria at pH 10.5. Consequently, long-lasting stable magnesia investment casting aqueous slurry can not be produced at the above pH. One

method to increase the lifetime of slurries is to prepare the slurries at higher pH values. As the pH goes up, the concentration of dissolving ions decreases (Figure 4) and consequently, slurries do not age as rapidly. For example, as shown in Figure 3, the lifetime of  $Y_2O_3$  slurry can be extended to about two months by simply adjusting the slurry pH to 11.

In slurries where silicon alkoxides are used as binder an increase in pH, as the result of dissolution of components and/or water moisture adsorption from the environment, normally reduces the slurry lifetime. Aging behavior of these slurries may differ depending on the amount of dissolution of components in the slurry. For example, rare earth ethyl silicate slurries may age very rapidly and become useless in less than a few hours. Alumina-based slurries age slower and in a similar environment may last a few weeks. On the other hand, in some slurries, such as zircon or fused silica slurries, the above types of interactions are even less severe and slurries may last for many months. In general, one may draw a symmetry between aqueous slurries and their ethyl silicate counterparts. Flours that produce aqueous slurries with short/long life, produce ethyl silicate slurries with relatively short/long life as well. Other non-silicon-based alkoxides normally go through hydrolysis and condensation reactions very rapidly <sup>(19)</sup>. For this reason, despite their high refractoriness, non-silicate alkoxides have not found popularity as binders in the casting industry.

Besides aging due to component interactions, there is yet another reason why investment casting slurries age <sup>(7)</sup>. Inorganic binders such as colloidal silica are chemically reactive. They permanently bond as the result of siloxane formation upon surface contact. While in the slurry, the possibility of direct surface to surface contact between colloidal silica particles is low due to the ionic cloud around each particle (diffused double layer). However, once these particles dry, their surfaces will contact and bonding will occur. Drying of particles may occur during many stages of the shell-making process. Any stage of the process that promotes formation of a slurry-air interface could potentially cause evaporation of surface water and bond formation between colliding particles. For example, after a part is dipped in a slurry pot, it is removed and the excess slurry allowed to drip off the shell, back into the pot. As the slurry is dripping back into the slurry pot, a large area of slurry-air interface is formed that promotes slurry aging.

The above two factors cause lost wax slurries to age over time and lose their usefulness. Slurry aging due to component interactions may be reduced by properly formulating the slurry. However, solutions to slurry aging due to the formation of slurry—air interface is not sufficiently explored and is presently handled only through careful quality control <sup>(7)</sup>. In a recent work, Yasrebi et al



have shown that slurry aging can be substantially reduced by the “Infiltration Method” in shell making processes <sup>(20)</sup>.

### ***b. Mechanical Properties***

Mechanical properties are among the most important properties in a shell mold. Without proper design of mechanical properties, quality and price of a cast part can drastically suffer. This is especially true for casting of high-temperature alloys, where molds normally have one or two facecoat layers of high refractory materials. Facecoat layers are thin and susceptible to stress cracks, high temperature erosion and deformation.

The main source of shell layer green strength is siloxane bonds formed by the condensation of silica binder. One way to increase the strength of a shell layer is to add more binder to the slurry. A series of zircon slurries were made with varying amount of silica binder. The exact formulation and procedure is shown elsewhere <sup>(20)</sup>. Test bars were then made and the green strength of the bars was measured.

The general trend in the green strength is shown in Figure 5. An increase in the concentration of silica binder results in an increase in green strength of the shell to a point. After a critical binder concentration, shell strength decreases. The reason for the existence of a maxima in the strength curve may be explained as follows <sup>(21-23)</sup>. Below the critical concentration, there is simply not enough binder between particles to bind particles efficiently. Above the critical concentration, due to a large concentration of binder in between flour particles, flours are unable to touch surfaces when the shell dries. Furthermore, as the binders in between the flour particles dry, a large amount of shrinkage occurs, producing microcracks that eventually contribute to a decrease in the strength. The curve in Figure 5 may be moved upward to some extent by optimizing a number of variables such as surface area, size and the morphology of binder or flour particles <sup>(21-23)</sup>.

High-temperature properties of a shell layer, such as hot strength and creep, closely follow the same trend observed for shell green strength, illustrated in Figure 5. Hot strength values also go through a maximum at the point of silica critical concentration. On the other hand, the creep curve goes through a minimum at the point of silica critical concentration <sup>(20)</sup>.

It is normally desirable to design slurries at the critical concentration of silica, where shell strength is at its maximum and creep is at its minimum value. However, if the reaction between the molten alloy and the relatively low refractory silica becomes a concern, then concentration of silica is reduced. An example of such a case is casting of Ti alloys (reaction 1). Facecoat slurries

for Ti shell molds have a very low concentration of silica binder, which increases the possibility of erosion, crack and deformation of the facecoat.

One may use an alternative shell-making method to substantially increase the green strength at lower silica binder contents. Test bars from zircon slurry with only 5 volume % colloidal silica binder were constructed. Dry bars were then infiltrated with colloidal silica for three hours. Some of the infiltrated bars with colloidal silica were infiltrated for a second time after being dried. The results are shown in Figure 5. Bars that were infiltrated once showed green strength of 1100 psi. Total amount of silica in the shell was calculated to be at 11 volume %. After the second infiltration, silica content went up to 16 v/o and green strength became 1650 psi. It is shown that when using the infiltration method, green strengths in excess of 3000 psi can be obtained <sup>(20)</sup>.

Reasons for the above increase in strength by the infiltration method can be speculated upon based on the explanation for the existence of a maxima in strength curve <sup>(20)</sup>. As the amount of binder in the slurry increases, the total bonding between flour particles increases and the green strength goes up. As it was discussed earlier, the bonding between particles increases only up to the point of maximum in Figure 5. As the slurry dries, some part of the binder will dry inside the cavity between particles and does not contribute to bond formation between particles. On the other hand, during the infiltration process, flour particles are already in contact and bonded together. Once the additional binder is infiltrated inside the porous shell, binder liquid is drawn to the neck region between particles due to capillary action. As the binder dries, it dries at the neck region and further increases bonding between particles.

## Summary

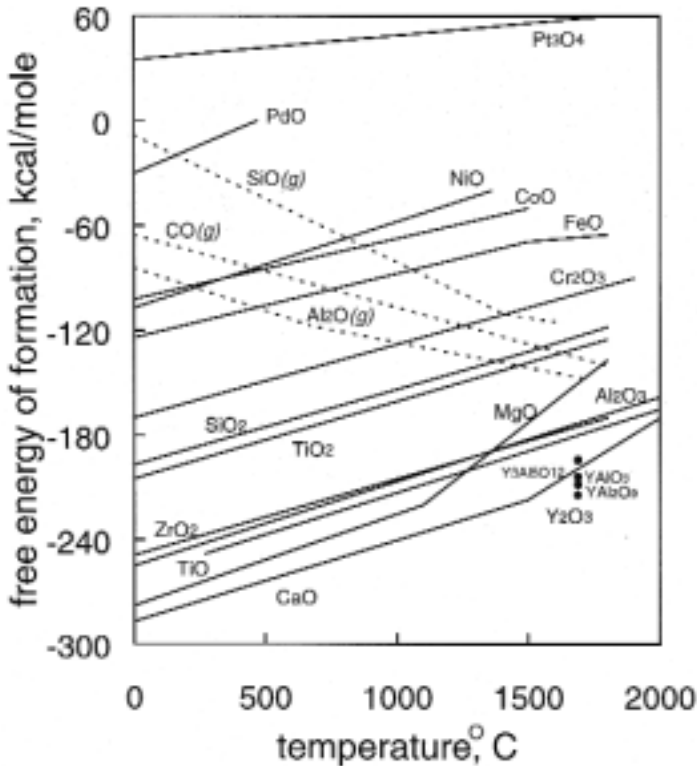
Ceramic molds for casting of high-temperature alloys have to satisfy certain requirements. Refractory materials in the mold should retain their chemical stability in contact with molten alloy. Mold materials, as a first order approximation, should have  $\Delta G_f^\circ$  comparable or preferably more negative than the oxides of molten alloy. In addition, the mold should have a high enough liquidus temperature in order to retain its mechanical stability at the cast temperature.

Besides materials requirements, proper processing of molds should also be exercised. Slurries should be prevented from excessive aging. Electrochemical properties of individual components in the slurry should be reviewed in order to ensure minimal component interactions. Slurry pots should be monitored regularly to prevent excessive aging due to binder agglomeration at the air-slurry interface. Finally, mechanical properties of the shell need to be designed

to ensure defect-free parts. Maximum strength and minimum creep can be achieved at the critical concentration of binder in the slurry. If it becomes desirable to reduce the amount of silica binder, then the infiltration method can be used to optimize strength and creep in a shell system.

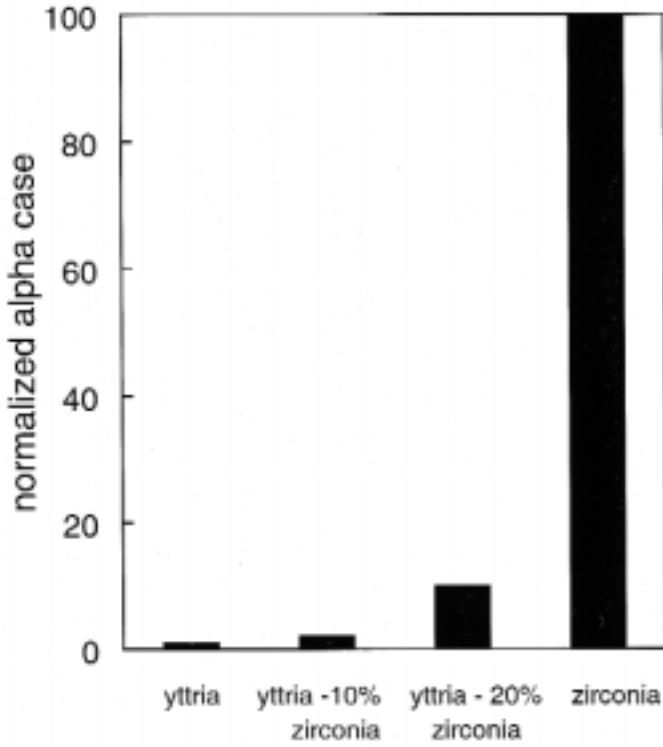
**Table 1** Melting temperature for selected metals and refractory oxides <sup>(24)</sup>.

<i>Metal</i>	<i>Melting Temperature, °C</i>	<i>Ceramic</i>	<i>Melting Temperature, °C</i>
Ir	2410	magnesia	2852
Ru	2310	zirconia	2700
Pt	1772	Calcia	2614
Ti	1660	zircon	2550
Pd	1554	yttria	2415
Fe	1535	lanthana	2307
Co	1495	alumina	2072
Ni	1455	titania	1830
Au	1064	silica	1720
Ag	961	calcium sulphate	1450



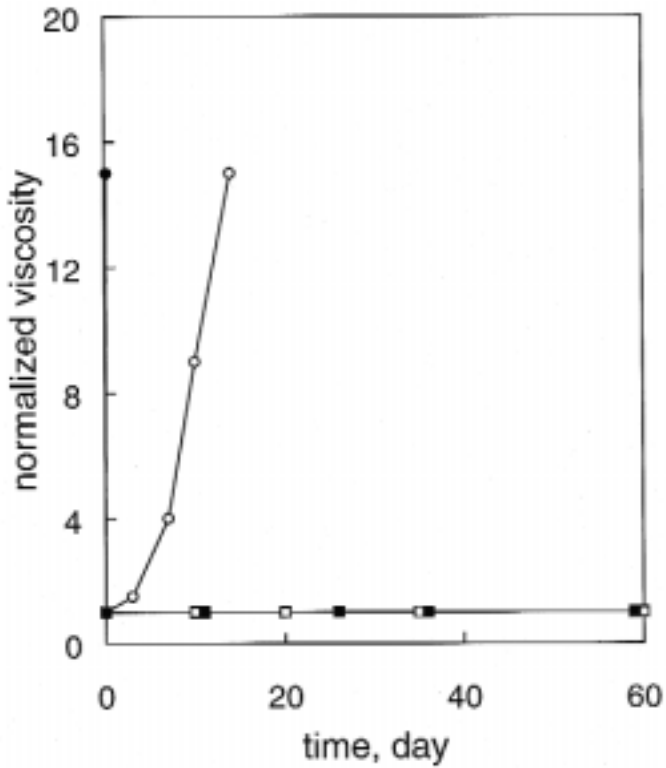
**Figure 1**

Free energy of formation for some refractory oxides, and the oxides of some of the high melting temperature metals <sup>(25-28)</sup>.



**Figure 2**

Normalized alpha case of one-inch Ti cast as a function of shell mold refractory. Yttria-zirconia refractories were fused <sup>(7)</sup>. Slurries were made with 5 weight % silica binder.



**Figure 3**

Normalized viscosity as a function of time. □ represents alumina-silica slurry at pH 10.5; ■ represents yttria-silica slurry at pH 11; ○ represents yttria-silica slurry at pH 10.5; and ● represents magnesia-silica slurry at pH 10.5.

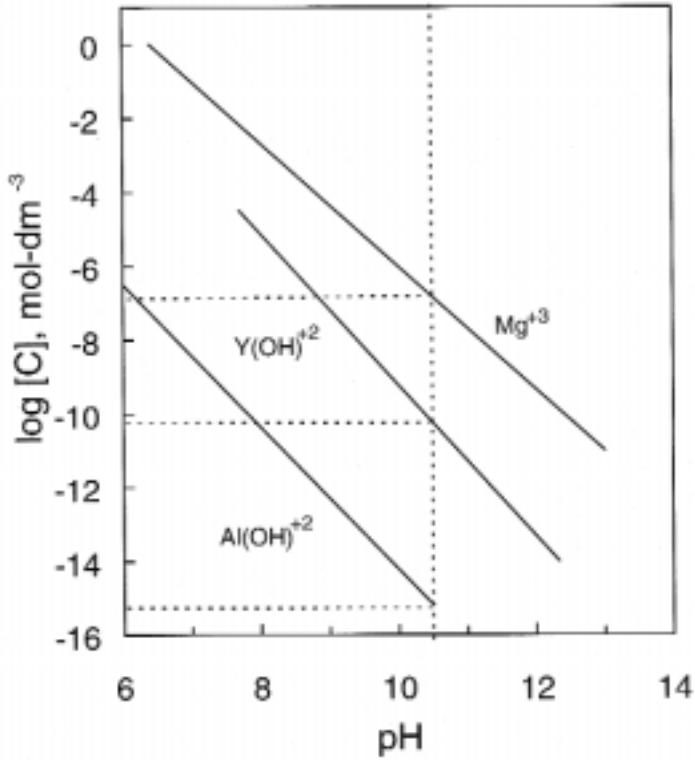
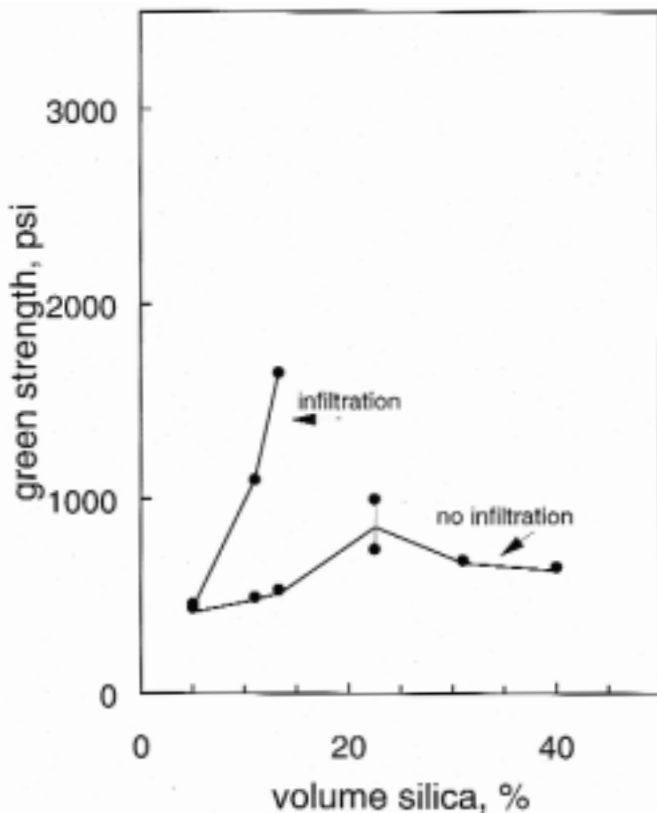


Figure 4 Ion concentration diagram as a function of pH.



**Figure 5**

Green strength as a function of volume concentration of silica in the shell. Infiltration line data points are green strength values obtained after shell made from slurry with 5 volume % silica was infiltrated with colloidal silica binder.

## References

- 1 O. Kubaschewski, "Thermochemistry of Metal-Refractory Interactions," Rev. Int. Hautes Temp. Refract., 3[3] 229-34 (1966).
- 2 C. Frueh, D. R. Poirier, M. C. Maguire and R. A. Harding, "Attempts to develop a ceramic mould for titanium casting - a review," Int. J. Cast Metals Res., 1996, 9, 233-239.
- 3 E. S. Lassow, P. R. Johnson, S. R. Whitaker and M. Guerra Jr., "Ceramic shell mold facecoat and core coating systems for investment casting of reactive metals," US Patent 4, 03,806.
- 4 R. C. Feagin, "Casting of reactive metals into ceramic molds," Sixth word conference on Investment Casting (1984).

- 5 T. S. Piwonka, "Reactions at the mold/metal interface in investment castings," ICI, 42nd annual technical meeting (1994).
- 6 R. L. Saha, T. K. Nandy, R. D. K. Misra and K. T. Jacob, "On the evaluation of stability of rare earth oxides as face coats for investment casting of titanium," *Metallurgical Transactions B*, Vol. 21B, 559-66, June 1990.
- 7 M. Yasrebi, W. W. Kemp, and D. H. Sturgis, "Aging of Aqueous Investment Casting Slurries, Causes and Solutions," in proceeding of the 46th annual technical meeting and exhibition of the Investment Casting Institute (1998).
- 8 I. C. Huseby and F. J. Klug, "Chemical compatibility of ceramics for directionally solidifying Ni-base eutectic alloys," *Am. Ceram. Soc.*, Vol. 58 No. 5, 527-35 (1979).
- 9 K. Maca and J. Cihlar, "Interaction between alumina ceramic cores and reactive metals," in proceeding of the 47th annual technical meeting and exhibition of the Investment Casting Institute (1999).
- 10 O. Kubaschewski, "Thermodynamic properties of double oxides," *High Temp.-High Pressures*, 4[1] 1-12 (1972)
- 11 G. M. Ingo, G. Chiozzini, V. Faccenda, E. Bemporad and C. Riccucci, "Thermal and microchemical characterizations of CaSO<sub>4</sub>-SiO<sub>2</sub> investment materials for casting jewellery alloys," *Thermochemica Acta* 321, 173-83 (1998).
- 12 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, "The NBS tables of chemical thermodynamic properties," *Am. Chem. Soc.* (1982)
- 13 LUDOX Colloidal Silica, Properties, Uses, Storage and Handling, Du Pont, Wilmington, DE.
- 14 D. J. Shaw, "Introduction to colloid and surface chemistry," Third edition, Butterworths (1980).
- 15 J. Li, "Wetting and interfacial bonding of metals with ionocovalent oxides," *J. Am. Ceram. Soc.*, 75 [11]3118-26 (1992).
- 16 C. J. Brinker and G. W. Scherer, "Hydrolysis and Condensation II Silicates," in *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Process*, Chapter 4, Academic Press (1990).
- 17 M. Yasrebi, M. Ziomek-Moroz, W. W. Kemp, and D. H. Sturgis, "The Role of Particle Dissolution in the Stability of Binary Colloidal Suspensions," *J. Am. Ceram. Soc.*, 79 [5]1223-27 (1996).
- 18 M. Yasrebi, W. W. Kemp, D. H. Sturgis, "Yttria-Zirconia Slurries and Mold Facecoats For Casting Reactive Metals," U.S. Patent # 5,407,001.
- 19 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, "Metal Alkoxide," Academic Press (1978).



- 20 M. Yasrebi, W. W. Kemp, and D. H. Sturgis, "Infiltration Method for Producing Investment Casting Shell," in proceeding of the 47th annual technical meeting and exhibition of the Investment Casting Institute (1999).
- 21 W. O. Roberts, "Colloidal Silica," in How to Avoid Shell Cracking, Investment Casting Institute (1989).
- 22 R. L. Rusher, Sr., "Strength Factors of Ceramic Shell Molds, Part I," *Cast Metal Res. J.*, Vol. 10, No. 4, pp. 149-53 (1974).
- 23 R. L. Rusher, Sr., "Strength Factors of Ceramic Shell Molds, Part II," *Cast Metal Res. J.*, **11**, No. 1, pp. 21-26 (1975).
- 24 *Handbook of Chemistry and Physics*, 70th edition, CRC Press (1989-1990).
- 25 H. J. De Bruin and S. P. S. Badwal, "Free Energy of formation of PdO by Impedance Dispersion Analysis," *J. of Solid State Chemistry* **34**, pp. 133-35 (1980).
- 26 J. Stuart Warner, "The Free Energy of formation of Palladium Oxide," *J. Electrochem. Soc.*, **114**, No. 1, pp. 68-71 (1967).
- 27 I. C. Huseby, F. J. Klug, "Chemical Compatibility of ceramics for directionally solidifying Ni-Base eutectic alloys," *J. Am. Ceram. Soc.*, **58**, No. 5, pp. 527-35 (1979).
- 28 R. A. Swalin, in *Thermodynamics of Solids*, 2nd edition, John Wiley & Sons (1972).